

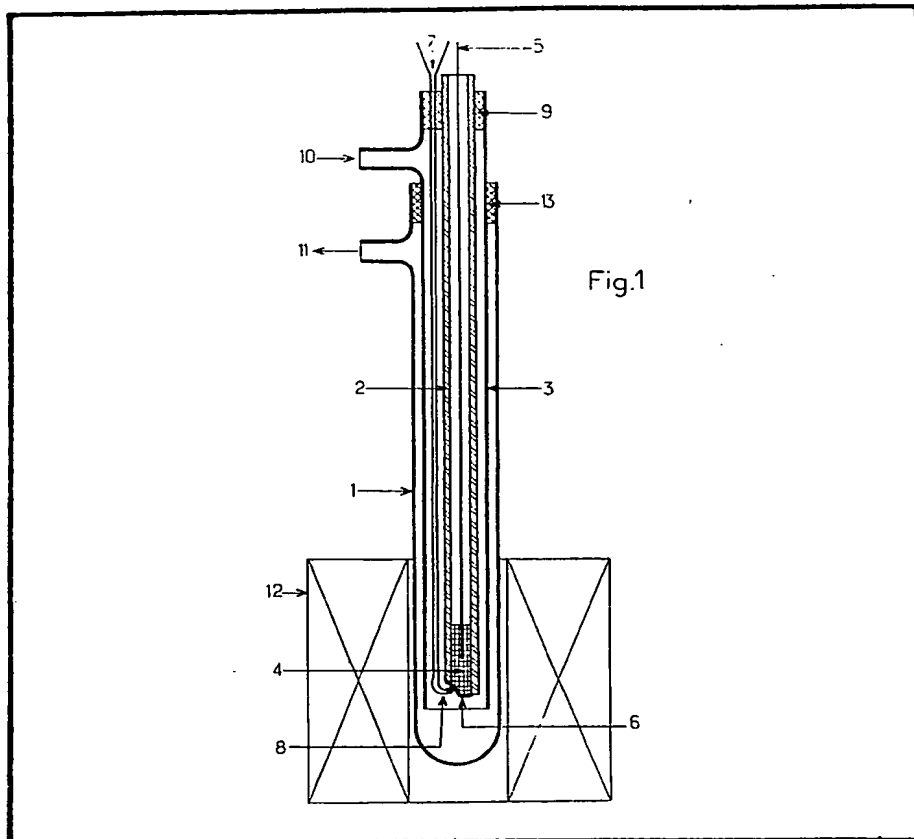
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(54) Electrochemical chlorine sensor

(57) An electrochemical chlorine sensor comprises a measuring electrode (6) formed from a compound of ruthenium, iridium, osmium, molybdenum or tungsten which is conductive at room

temperature. The compound is preferably an oxide and/or halide, and preferably a chloride. Preferred compounds are RuO_2 and/or RuCl_3 . The sensor preferably comprise a solid electrolyte 4 conducting by chloride ions and a solid reference which may be a metal/metal halide mixture or a mixture of metal halides.



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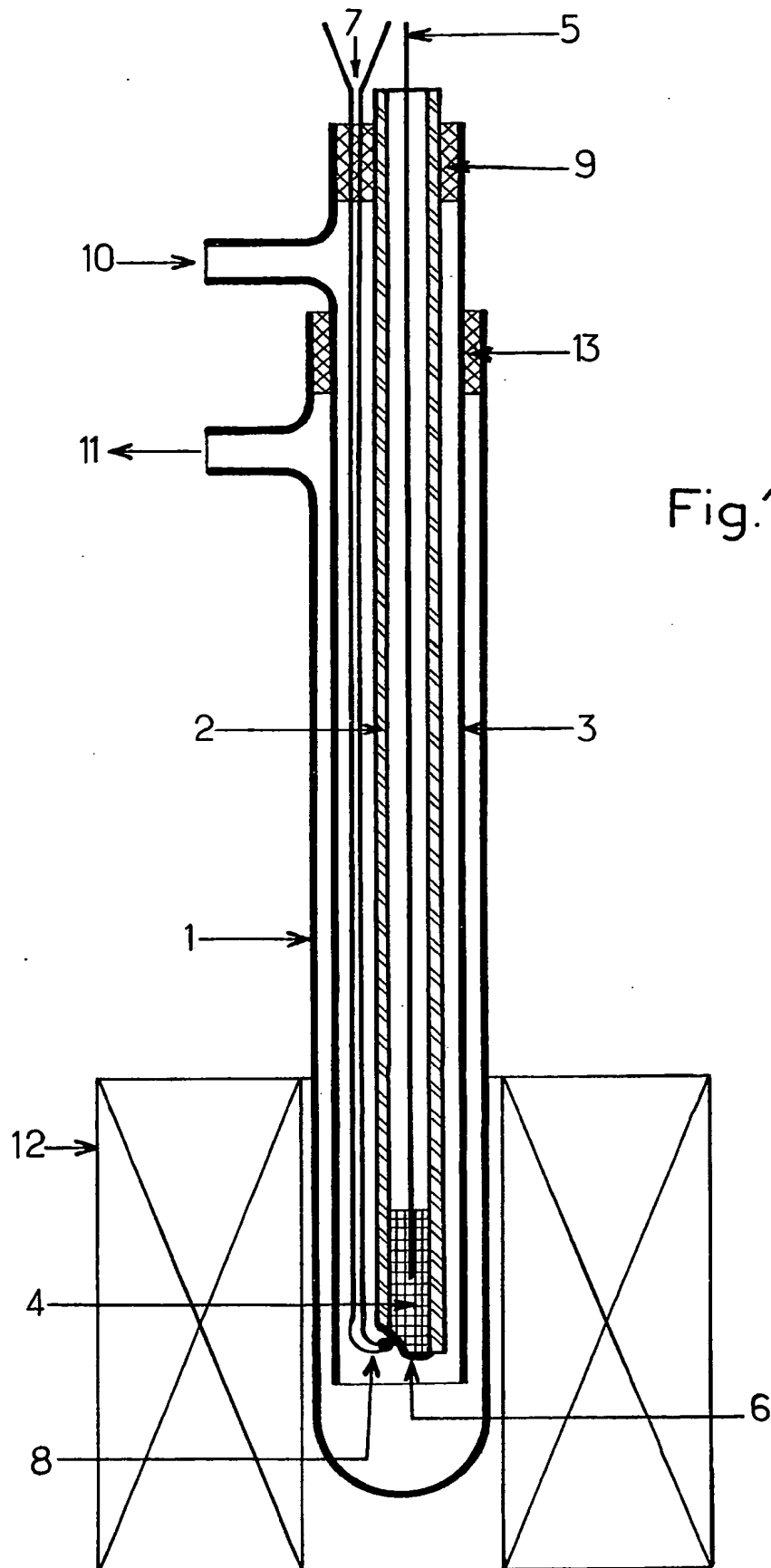
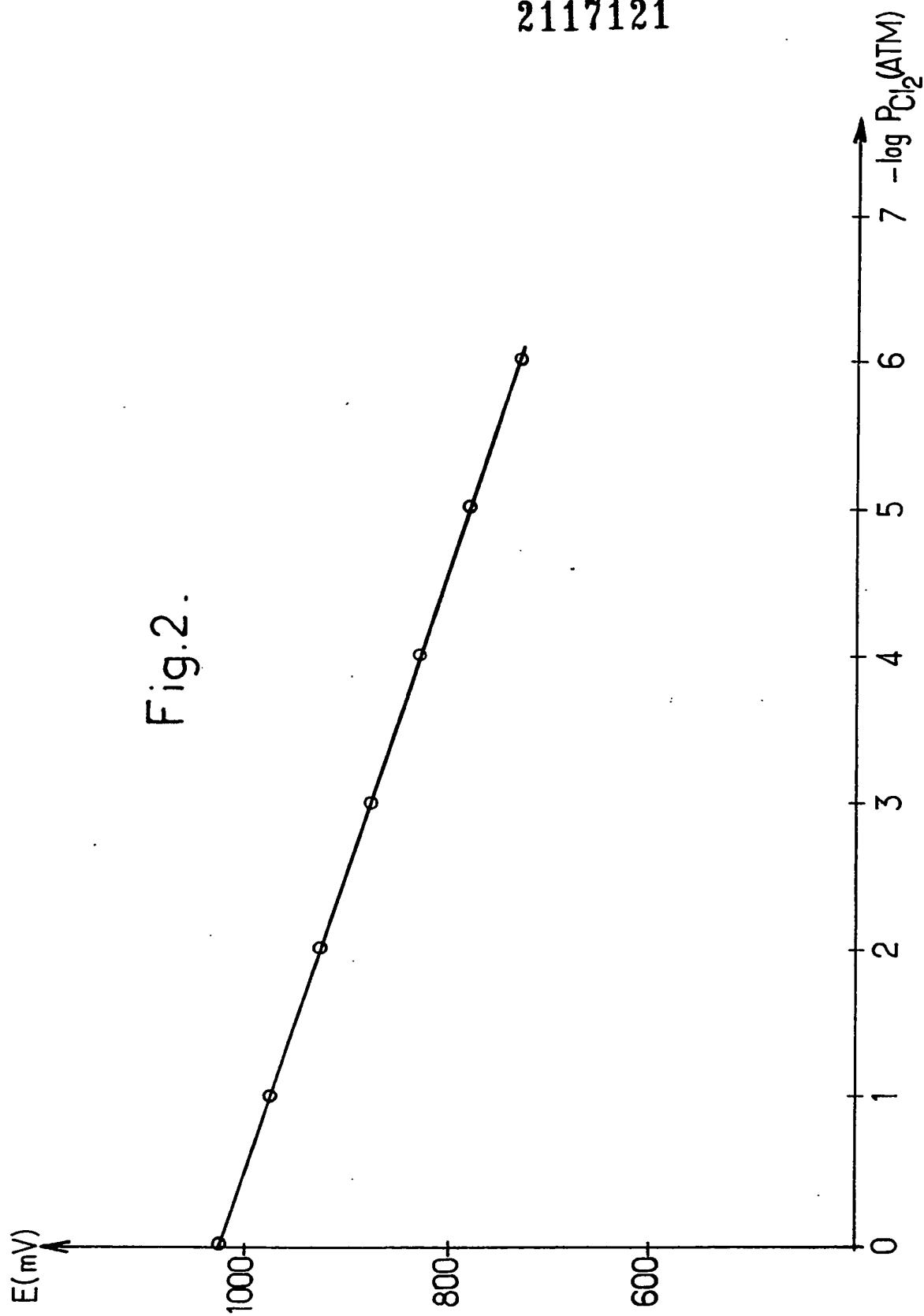


Fig.1.

Fig.2.



SPECIFICATION

Electrochemical chlorine sensor

The present invention relates to an electrochemical chlorine gauge and the application thereof for measuring partial chlorine pressures, in particular in gas mixtures.

It relates more specially to a chlorine gauge with internal reference and solid electrolyte.

Such a gauge operates as a galvanic cell formed of an electrochemical chain with a solid electrolyte in contact with two electronic conductors, comparable to electrodes, located respectively in different environments or compartments.

One of these electrodes, or reference electrode, is located in a so-called reference compartment where the chlorine pressure may be determined by a chemical system or a standard gas mixture.

The second electrode, or measuring electrode, is external to the reference compartment and, in operation, in contact with the gas medium to be analyzed. By "measuring compartment" is meant this measuring electrode and the medium to be analyzed.

These reference and measuring electrodes are furthermore in contact with an electrolyte containing a chloride with ionic conductivity provided predominantly or totally by Cl^- ions, or by interstitial cations.

The presence of chlorine in the oxidized state and of chlorine in the reduced state in contact with the electrodes of each of these reference and measuring compartments allows a reaction at these electrodes leading to the appearance of a potential difference. This potential difference E obeys NERNST's law, namely:

$$E = \frac{RT}{4F} \ln \frac{P_m}{P_r}$$

where

E represents the potential difference in volts,
 R the constant of the perfect gases,
 T the temperature of the assembly in degrees Kelvin,
 F Faraday's constant,
 P_m the chlorine pressure in the measuring compartment,
 P_r the reference pressure in the reference compartment.

At a fixed temperature, with P_r established, from this relationship P_m can be deduced from the measurement of E .

Experimentally, one of the co-inventors in Solid-State Ionics 1 (1980) 343—354 had studied, with other associates, the behavior of an oxygen gauge as a chlorine gauge.

In the gauge described, the solid electrolyte was formed by strontium chloride SrCl_2 doped with potassium chloride KCl and optionally with strontium oxide SrO .

The measuring electrode was formed from graphite or vitreous carbon and the reference

system was formed by a silver electrode, embedded in silver chloride dissolved in the electrolyte or by a compressed powder of an Ag and AgCl mixture in contact with the electrolyte and connected to a silver filament.

The results obtained showed good sensitivity of the gauge in a temperature range from 100 to 450°C for partial chlorine pressures greater than 10^2 Pa.

However, the advantage can be well understood of having systems with improved performances allowing, more especially, very low chlorine pressures to be detected and measured.

The study of this problem by the inventors led them to seek new materials usable in constructing the measuring electrodes.

The work carried out has in fact shown that by using certain types of materials, it was possible to carry out chlorine pressure measurements with remarkable accuracy even at low chlorine pressure.

It is then an object of the invention to provide means for forming chlorine gauges with high performances, even at low chlorine pressure.

In another aspect, it relates to a chlorine gauge equipped with these means and different methods of constructing such a gauge.

According to yet another aspect, it relates to the application of these gauges for measuring the partial chlorine pressure in gas media.

For forming a measuring electrode, usable in a chlorine gauge, recourse is had in accordance with the invention to a material comprising a derivative of a transition metal, conductive from room temperature, this transition metal being chosen from the group comprising Ru , Ir , Os , Mo and Ti .

Advantageously, this derivative is formed by an oxide of the transition metal and/or a halide, more especially a chloride. These compounds with then correspond to RuO_2 , IrO_2 , MoO_2 or TiO , or the corresponding halide.

According to one aspect of great interest, these materials which may be finely divided present high catalytic properties for transferring the chlorine into chloride ions and conversely. These are due to the presence of free electrons in these materials (the electrons of the p and d orbitals of the orbitals of the metal are not all engaged with the oxygen in the form of oxide ions). These materials, especially when they are saturated at a given pressure, allow then measurements of partial chlorine pressures to be made with great accuracy, even when these pressures are very low.

According to one arrangement of the invention, the oxide of the transition metal is obtained by thermal decomposition of the corresponding chloride and, if need be, is then doped with chlorine.

For reasons essentially related to commercial availability, RuO_2 and/or RuCl_3 are preferred for forming a measuring electrode for a chlorine gauge.

RuO_2 is advantageously obtained by thermal decomposition of RuCl_3 .

In this respect an ink is preferably used formed by an alcohol solution (with for example

- 5 methanol, propanol or butanol) at about 0.02 to 0.1 mole l^{-1} of RuCl_3 . Aqueous solutions may also be used.

- 10 The invention also relates to a chlorine gauge with internal reference and solid electrolyte of the type mentioned above in which the measuring electrode is formed from a material such as defined above.

- 15 This gauge comprises in this case a measuring compartment in which the gas to be analyzed will come into contact with the measuring electrode, advantageously under conditions allowing a pressure of equilibrium to be reached rapidly. The measuring electrode, formed from a derivative of a transition metal as defined above, is in contact
20 with a metal conductor not reacting on the chlorine under the measuring conditions. It is also in contact with the electrolyte and is advantageously in the form of a layer covering at least a part of the external surface of the electrolyte.

- 25 The solid electrolyte defines a part of the reference compartment. This electrolyte may contain in the dissolved state a part of the system for establishing a reference chlorine pressure or may even be formed by this part.

- 30 The internal reference compartment is hermetically sealed and comprises a chemical system, in which may participate the reference electrode, for the rapid establishment of a pressure of equilibrium, over a wide temperature range.

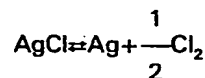
- 35 Advantageously, the measuring electrode used catalyzes the oxidation of the Cl^- ions and facilitates equilibrium of the reaction occurring at the electrodes, and this at chlorine pressures as low as 10^{-1} Pa, even lower. It is further particularly remarkable that, even at these low pressures, the response times observed are of the order of a minute.

- 40 According to one embodiment of the invention, the chlorine gauge comprises a reference compartment in the form of an hermetically sealed tube or sheath formed from a material, inert with respect to chlorine and stable at high
50 temperatures, for example from alumina to mullite.

- This tube comprises the reference electrode and the system for establishing a given chlorine pressure, of which the electrode may possibly
55 form part.

- This system may be formed by a standard gas mixture, a metal-chloride mixture such as $\text{Ag}-\text{AgCl}$, $\text{Ni}-\text{NiCl}_2$, $\text{Fe}-\text{FeCl}_2$ or a mixture of two chlorides of the same metal, for example $\text{CuCl}-\text{CuCl}_2$ or any other system appropriate for
60 implementing the invention.

- The partial reference pressure may be easily provided by the dissociation equilibrium of silver chloride into chloride and into silver according to
65 the equation:



- 70 The establishment of this equilibrium is rapid, particularly at low temperature. Furthermore the standard free enthalpy values ΔG_T° of this reaction are accurately known, so that the partial chlorine pressure which is formed at the reference electrode may also be known with great accuracy.

- This latter is then formed from a silver filament placed in the silver chloride inside the tube, in
75 contact with the electrolyte, forming a separate reference system.

- Alternatively, the reference electrode penetrates into the very heart of the electrolyte in which is dissolved the chloride of the metal
80 corresponding to the metal forming this electrode.

- Alternatively again, the silver wire plunges into the very heart of the electrolyte which is here no other but pure or doped silver chloride.

- The solid electrolyte used is advantageously
85 chosen from materials with relatively high Cl^- ion conductivity at moderate temperatures.

- The electrolyte may also be chosen from pure or doped cationic conducting chlorides.

- Solid solutions of pure or doped alkaline and/or
90 alkaline-earth metal halides prove particularly appropriate.

- A preferred halide is formed by strontium chloride. Strontium chloride doped with potassium chloride at the rate of 0.1 to about 2%,
95 preferably about 1%, is more specially used. It is also advantageous to use as electrolyte AgCl , pure or doped for example with CdCl_2 or PbCl_2 . PbCl_2 alone may also be used.

- Other solid solutions are suitable for carrying
100 out the invention and could be easily chosen by a man skilled in the art such as calcium chloride-potassium chloride, barium chloride-potassium chloride.

- As above mentioned, the reference
105 compartment is hermetically sealed. It is in fact necessary, for the accuracy of the measurements, to avoid any introduction of elements from the outside atmosphere into the reference compartment. It is also necessary for this
110 compartment to be maintained at a uniform temperature. It is in fact advisable to avoid any variation of the chlorine pressure fixed by the reference system because of the existence of a temperature gradient inside the compartment and to avoid condensation of the chloride or of the
115 metal which, at a given temperature would be sufficiently volatile to evaporate and condense in the part of the reference compartment which would be colder.

- To ensure hermetic sealing, the reference
120 compartment is advantageously sealed with an appropriate material which is sealed to the walls defining the compartment. The tube or sheath is also sealed at the outlet of the reference electrode
125 from the compartment, and between the different parts possibly forming the sheath. This sealing is provided by a material which is sufficiently

resistant to the temperatures met with in use of the gauge and to chlorine. Among appropriate materials, pyrex glass may be mentioned.

- The gauges thus formed are particularly accurate and sensitive even to chlorine pressures of the order of 10^{-2} Pa or less. Their response time to the variation of the composition of the gas to be studied is very short. Furthermore, they have a remarkable mechanical strength and high thermal shock resistance.

- The gauges deliver a reliable signal between about 100 and 700°C (above, AgCl reference or electrolyte AgCl melts). In practice, they are operated between about 150 and 260°C.

- These properties are further improved when the gauges of the invention are constructed in the form of small-sized apparatus.

- Advantageously, apparatus may be constructed of about 10 to 20 cm in length and about 1 to 4 cm in width.

- Furthermore, the miniaturization of the gauges of the invention allows an isotherm reference compartment to be formed and thus the errors resulting from temperature gradients to be removed, which errors can only be eliminated with difficulty with gauges of larger volume.

- To illustrate the invention, a preferred embodiment of a chlorine gauge has been described hereafter with reference more especially to the drawings in which:

- Figure 1 is a schematic view in partial section of a gauge constructed according to this preferred embodiment; and

- Figure 2 represents the variation of the electromotive force of such a gauge, at 200°C, as a function of the logarithm of the inverse of the measured chlorine pressure.

- In Figure 1 there is shown a miniaturized gauge comprising an external pyrex glass tube 1 and two internal tubes 2 and 3 extending axially into tube 1, the upper part of 2 being engaged and held in the upper part of 3, the length of these tubes 2 and 3 thus fitted together being greater than that of 1.

- Tube 2 is made from alumina or mullite. It contains in its upper part engaged in 3 the electrolyte 4. This electrolyte is advantageously formed by SrCl_2 doped with 0.1% of KCl; or AgCl doped with CdCl_2 and containing 0.1% of dissolved AgCl.

- This tube 2 also contains the reference system formed by a silver filament 5 penetrating into the electrolyte 4. This filament is connected outside to a device not shown. The measuring electrode is formed by a layer 6 of RuO_2 deposited on the outer part of the electrolyte and is in contact with a current lead-in 7 formed by graphite, vitreous carbon or any other metal type conductor which does not react on the chlorine under the measuring condition. In practice, the end of the current lead-in 7 is formed by the bulb 8 of a thermocouple (Pt-Pt Rh 10%). Besides its voltage taking function this thermocouple also serves for taking temperature. It is placed in parallel with tube 2 and projects sealingly at the level of the

seal 9. The bulb (or end) 8 of the thermocouple is crimped or held under pressure on the RuO_2 electrode 6.

- Tube 3 comprises in its upper part a gas inlet 10, this gas, after passing close to the measuring electrode 6, is discharged through opening 11. The temperature is maintained by an oven 12.

- Generally, sealing and centering of the parts are provided by Teflon (R.T.M.) seals or rings. With seals 9 and 13, tube 2 is held in tube 3, and tube 3 in tube 1.

- The gauge described is more specially intended to operate in a confined chlorine atmosphere requiring gas circulation.

- For detecting chlorine in a non confined atmosphere (possible leaks close to centers producing or using this gas), the different enclosures described (tubes 1 and 3, openings 10 and 11) are no longer valid, only the electrochemical element 2 remains with the electric lead-ins and oven 12. The circulation of the gas takes place by convection.

- In the embodiment shown in figure 1, gauges of about 15 cm in length and about 2 cm in diameter will be formed having a total volume of about 25–30 cm^3 . In these gauges, the diameter of the strictly electrochemical part is from 5 to 6 mm.

- The electrolyte-electrode assembly may be formed in the following way:

- The electrolyte containing the reference salt AgCl (ex. of a ponderal composition SrCl_2 99.8%, KCl 0.1%, AgCl 0.1%) is melted in an alumina crucible. The end of the alumina tube containing a silver wire is then plunged in the molten salt.

- For obtaining cells in which AgCl doped with CdCl_2 or PbCl_2 forms the electrolyte, the procedure is as follows: melting of AgCl and CdCl_2 or PbCl_2 at 480°C and introduction of the alumina tube containing the silver wire. After withdrawal and cooling, a ruthenium chloride film is deposited on the electrolyte flush with the end of the tube.

- According to another embodiment, the reference system of the gauge is outside the electrolyte and not in the electrolyte.

- Such a gauge is prepared as follows:

- a) The end of a wire silver is made flatted, a small circular plate of about 2mm being formed for example. The wire is then put into a tube (this tube being for example like tube 2 but containing no electrolyte) so as the tube be obturated.

- The obturated end part of the tube is heated and put into a crucible containing molten AgCl.

- The tube walls and the plate are then recovered by molten AgCl

- b) Besides, a small amount of a sintered or monocrystalline electrolyte such as above mentioned (excepted of course AgCl) is preheated at about 480°C.

- c) The plane face of the preheated electrolyte is deposited on the silver plate recovered with molten AgCl and allowed to cool. AgCl becomes solid, obturates the tube end part and sticks the electrolyte on the silver plate.

As above mentioned, a RuCl_3 film is deposited on the electrolyte, previously cleaned for example by washing. This procedure can be carried out on substrates other than the alumina tube and for example on a plate. It will be noted that the processing of this embodiment is made easier by the fact that, once melt and cooled, AgCl , forms a glue and is capable of insuring a good etancheity.

The study of the performances of gauges of this type have given the following results.

a) Operation of the reference electrode

In a temperature range from 50°C to 460°C , it was verified that the potential difference measured when the chlorine pressure is fixed for example at 10^5 Pa and 10^2 Pa, corresponds exactly to that derived from the thermodynamic data of formation of silver chloride (ΔG_f°). Numerous tests have confirmed the reliability of the $\text{Ag}-\text{AgCl}$ reference system in this temperature range.

b) Study of the response of the apparatus to different partial chlorine pressures

It has also been verified that, under the above fixed temperature conditions, the potential difference E follows perfectly NERNST's law for chlorine pressures from 10^5 to 10^{-1} Pa and even less. The results obtained at 200°C are shown in figure 2 in which the variation of the electromotive force E in millivolts of the gauge is shown as a function of the logarithm of the inverse of the chlorine pressure in $\text{Pa} \times 10^{-5}$. These values are independent of the carrier gas used which may be a neutral gas such as argon or nitrogen or else oxygen or even air.

For lower chlorine pressures, it is important for the accuracy of the measurements that the carrier gas does not contain any impurities.

c) Study of the response time of the gauge

The time required for the potential difference to change when the chlorine pressure changes rapidly from a value of P_1 to $P_{1/10}$ is of the order of a minute. The results of tests carried out at 200°C are shown by way of example in the following table:

<i>Partial pressure ranges of Cl_2 (in Pa)</i>	<i>Response times (95% of the value)</i>
$10^4 \pm 10^3$	15s
$10^2 \pm 10^1$	60s
10 ± 10^{-1}	

The whole of these results show the remarkable sensitivity of chlorine gauges of the invention even at very low chlorine pressure. These gauges are therefore especially suitable for measuring partial chlorine pressures over a wide pressure range and advantageously allow very low chlorine contents in gas media to be detected and measured.

Claims

1. Application to the construction of a measuring electrode for a chlorine gauge of a material comprising a derivative of a transition metal, conductive from room temperature, this transition metal being chosen from the group comprising Ru, Ir, Os, Mo and Ti.
2. The application according to claim 1, characterized in that the derivative of the transition metal is an oxide and/or a halide, more especially a chloride.
3. The application according to claim 2, characterized in that the oxide of the transition metal is obtained by thermal decomposition of the corresponding chloride and, if need be, is then doped with chloride.
4. The application according to any one of claims 1 or 2, characterized in that the derivative of the transition metal is formed by RuO_2 and/or RuCl_3 .
5. The application according to any one of claims 1 to 4, characterized in that RuO_2 is obtained from an ink formed by an alcohol solution of RuCl_3 , subjected to a thermal decomposition treatment.
6. A chlorine gauge with internal reference and solid electrolyte, characterized in that it comprises:
 - a measuring compartment in which the gas to be analyzed will come into contact with the measuring electrode, under conditions allowing a pressure of equilibrium to be rapidly reached, the measuring electrode, formed from a material according to any one of claims 1 to 5, being in contact with a metal conductor not reacting on the chlorine under the measuring conditions and also in contact with the electrolyte;
 - a solid electrolyte whose conductivity is essentially provided by mobility of Cl^- ions, defining a part of the internal reference compartment and possibly containing in the dissolved state a part of the system for establishing the reference chlorine pressure or be formed by this part;
 - an hermetically sealed internal reference compartment comprising a chemical system in which may participate the reference electrode for rapidly establishing a reference chlorine pressure over a wide temperature range.
7. The gauge according to claim 6, characterised in that the derivative of the transition metal used for forming the measuring electrode is in the form of a layer covering at least a part of the outer surface of the electrolyte.
8. The gauge according to claim 6 to 7, characterized in that it comprises in combination, as reference system, a metal-metal chloride mixture or a mixture of two chlorides of the same metal, as electrolyte an alkaline-earth halide, pure or doped with an alkaline halide, or else the metal chloride forming a part of the reference system, this chloride being pure or doped, or else another pure or doped metal halide and, as measuring electrode, an RuO_2 and/or RuCl_3 coating of the solid electrolyte.

9. The gauge according to claim 8, characterized in that it comprises, in combination, an Ag—AgCl reference system with pure AgCl or AgCl dissolved in the electrolyte, as electrolyte
- 5 SrCl₂ pure or doped with KCl, AgCl pure or doped with CdCl₂ or PbCl₂, or else PbCl₂, and an RuCl₃ and/or RuO₂ coating of the solid electrolyte.
10. The gauge accordig to claim 10, comprising a reference system Ag—AgCl outside the electrolyte having a silver wire with a flattened end part on which are successively applied molten AgCl, the electrolyte, which is different from AgCl, and the material forming the measuring electrode.
- 15 11. The gauge according to any one of claims 1 to 10 constructed in miniaturized form.

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